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# REASONS FOR THE FORMATION OF CORDS IN MELTING ELECTROVACUUM STRONTIUM GLASS IN A FLAME TANK GLASSMELTER OF NEW DESIGN

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The reasons for the formation of cords in melting electrovacuum strontium glass have been identified. The implementation of the measures proposed has made it possible to improve the product quality.

The progress in TV and computer engineering is related to stricter requirements imposed on the quality of electrovacuum glass. At the same time, the purpose is to obtain higher efficiency, lower production cost, and decreased fuel consumption.

In 2001 a new tank furnace for melting strontium glass was constructed for the Ekranas company. The furnace was designed by the Tekhneglass Company and replaced the old furnace that had been functioning for nearly nine years. Electrovacuum glass produced in the old furnace did not have a sufficiently high x-ray absorption coefficient and failed to meet international standards.

The new tank furnace has provided conditions for melting better-quality electrovacuum strontium glass with an increased content of BaO, SrO, $ZrO_2$, and $Sb_2O_3$ and a higher x-ray absorption coefficient. However, two years of producing electrovacuum glass of the new composition have witnessed the formation of a substantial quantity of new defects in making glass screens that had not existed before, namely, drop-shaped cords in the form of clear drops of size 1 – 3 mm that appear light-colored in an illuminated screen and frequently have round filaments (Fig. 1).

The methods of electron microscope and x-ray-fluorescence analysis established [1] that the clear heterogeneous drop-shaped inclusions in strontium glass are incompletely melted minerals containing solid solutions of potassium, sodium, and barium feldsparoids. Nearly half of the cords investigated do no contain zirconium oxide. The content of $Al_2O_3$ in all cords exceeds more than 10 times the content of this oxide in the bulk of the experimental glass melt. The cords also have an increased content of $K_2O$ and $Na_2O$; furthermore, increased quantities of $Al_2O_3$ or $ZrO_2$ are also found around the cords.

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As the number of screens rejected for this defect amounts to 8 – 10% of the total quantity of the product, the problem of decreasing or eliminating these cords becomes essential for the production of television screens.

To solve this problem, it is primarily necessary to identify the reasons for the formation of this new type of defect in the strontium glass for screens. Some glass manufactures believe that the main reason for the emergence of cords in glass is the melting of stalactites formed in the melting zone in the reactions between volatile alkaline batch components and the refractory material of the furnace roof and walls and subsequent penetration of melted stalactite drops on the glass melt surface, but this opinion elicits certain doubts.

The roof of the new furnace is insulated by the dinas refractory material; therefore, it is hard to imagine that the volatile components of the batch (which contains only 2% $Al_2O_3$) and dinas ($SiO_2$) can form difficultly soluble aluminosilicate stalactites on the roof surface. If the origin of cords were related only to the erosion of wall refractories under the effect of glass melt and the reaction between the alkali vapors of the batch and the same refractoriness, it would be hard to explain the fact that nearly half of the cords do not contain $ZrO_2$ that is present in substantial quantities

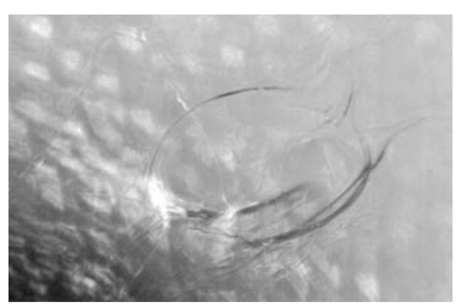

**Fig. 1.** Transparent drop-shaped cords with rounded filaments.



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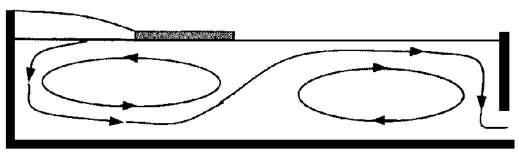

**Fig. 2.** Ideal two-dimensional mathematical model of melt flows in a glass-melting furnace with a neck.

(30 – 40%) in the refractory wall materials in the glass-melting zone of the new glassmelter.

In our opinion, the reasons for the formation of cords in screen glass are many and are related not only to the above mentioned processes but also to the modified furnace design, the glass composition, and the batch preparation method

Let us consider these factors in more detail.

The nature of the technological and convective glass melt flows depends on the design specifics of the glass-melting furnace, the time the glass melt stays in the high-temperature zones, and accordingly, the quality of melting and homogenization of the glass melt. The convection flows have a significant effect on some defects of glass, starting with microstructural inhomogeneous Griffith areas and ending with macroscopic insoluble inclusions [2 – 4].

The main method for the elimination of glass defects is correct organization of the melt flow routes in the longitudinal and lateral directions of the furnace tank. The melt should stay for a sufficient time in the zones of batch melting, clarification, and homogenization of the melt, which is necessary for the completion of all stages of glass melting. The spatial fixing of the quellpunkt plays a significant role in ensuring the required motion of convection flows. This may be achieved by installing a refractory barrier, air-lift systems, or additional electric heating of the bottom layers of the melt in the quellpunkt zone [5]. Fixing the quellpunkt by means of the flame in a regenerative tank furnace is the least effective for obtaining a desirable type of convection flows [5, 6]. It is generally known that with correct spatial fixation of the quellpunkt, the glass melt in the form of the classical "figure eight" flows from the site of batch charging toward the furnace neck providing for the rise of the bottom glass layers in the quellpunkt zone with the highest melting temperatures. Figure 2 shows an ideal two-dimensional mathematical model of the glass melt flows obtained for a glass-melting furnace without a barrier and with flame heating of the quellpunkt zone [7].

However, the real motion of glass melt flows in this type of the furnace obtained in 3D computer modeling [3] turned out to be different (Fig. 3). Part of the melt with lower temperatures and with higher density and kinetic viscosity values sinks near the edge side of the tank and moves rectilinearly straight to the neck without rising in the quellpunkt zone.

As the melting tank depth has been increased by 200 mm and the furnace bottom thickness has decreased by 100 mm (compared with the previous tank furnace), the risk of the melting and homogenization in such flows being delayed becomes high. The absence of a barrier in the batch melting zone and a significant increase in the cross-sectional area of the neck and the specific glass melt output contribute as well to this particular motion of a part of the bottom layers [8].

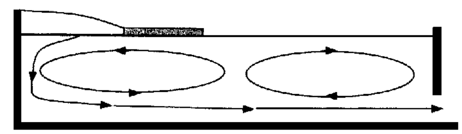

**Fig. 3.** Three-dimensional mathematical model of melt flows in a glass-melting furnace with a neck.

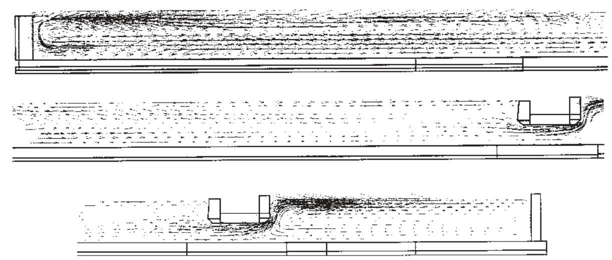

**Fig. 4.** Three-dimensional computer model of glass melt flows in the new furnace.

A 3D computer model (Fig. 4) constructed on the basis of the operating parameters of the new furnace of the Ekranas company for melting electrovacuum strontium glass has confirmed that the flow migration is analogous to the above-mentioned.

A substantial part of the melt cooled to 1573 – 1483 K in the edge part of the furnace sinks under the effect of the relatively cool batch layer and becomes even cooler as a consequence of heat exchange with the ambient medium (approximately by 70 K). The more viscous and denser melt flows rather fast (due to the higher velocity of the production flow, absence of barriers, and twice as large cross-sectional area of the flow) along the bottom zone of the furnace and passes beneath the quellpunkt zone without rising in this zone, which has higher temperatures than other sites.

The analysis of phase diagrams of alumosilicates under the atmospheric pressure indicates that the temperatures of 1380 – 1423 K are the melting points of high-temperature sanidine $(K, Na)AlSi_3O_8$ and albite $NaAlSi_3O_8$, which with increasing temperature can form solid solutions with barium aluminosilicates (hyalophane $(K, Ba)Al(Al, Si)_3O_8$ and celsian $BaAl_2SiO_3$) present in the melt.

A comparison of the chemical compositions of larger (1 – 3 mm) cords, strontium glass, and refractory materials of the furnace indicates that the emergence of some cords can be attributed to the erosion of refractory wall materials and their reaction with the alkali vapors of the batch at high temperatures. This is evidenced by a significantly higher (more than 10 times) quantity of $Al_2O_3$ in the cords and the pre-

**TABLE 1**

| Oxide | Mass content, %, in glass* produced | |
|---|---|---|
| | in the old furnace | in the new furnace |
| $SiO_2$ | 63.25 ± 0.8 | 61.70 ± 0.5 |
| $Al_2O_3$ | 3.85 ± 0.6 | 2.00 ± 0.2 |
| CaO | 1.80 ± 0.5 | – |
| BaO | 6.50 ± 0.6 | 8.70 ± 0.3 |
| $Na_2O$ | 7.20 ± 0.6 | 7.80 ± 0.4 |
| $K_2O$ | 7.85 ± 0.6 | 7.60 ± 0.3 |
| ZnO | – | 0.50 ± 0.2 |
| $TiO_2$ | 0.40 ± 0.1 | 0.40 ± 0.1 |
| $CeO_2$ | 0.15 ± 0.1 | 0.30 ± 0.1 |
| $Sb_2O_3$ | 0.40 ± 0.1 | 0.25 ± 0.1 |
| $ZrO_2$ | – | 1.50 ± 0.2 |
| SrO | 8.35 ± 0.5 | 9.30 ± 0.3 |
| $F_2$ | 0.25 ± 0.1 | – |

* $Fe_2O_3$ content not more than 0.2%.

sence of $ZrO_2$ in their compositions, as well as an increased quantity of $K_2O$ and $Na_2O$.

In these conditions clear granular aggregates of kalsilite $2[KASiO_4]$ or kaliophilite $KAlSiO_4$ can be formed, which have been identified in the mineral composition of some cords.

However, a substantial part of the cords do not contain $ZrO_2$, whereas enhanced quantities of $Al_2O_3$ and $K_2O$ are observed in the cords of size 0.5 – 1.0 mm and in the nearest boundary glass layers. As the composition of these cords has little correlation with possible products of interaction with the roof stalactites or with refractory wall materials, it can be assumed that such heterogeneities arise due to incomplete melting and homogenization of the batch components.

The introduction of screw feeders, the increase in the height of the first two sections of the furnace roof, covering the roof seals with refractory plates, covering the tank bottom with refractory tiles, and cooling the walls of the tank zone in which the melt directly contacts the refractory materials, i.e., the design solutions that were used in the new tank furnace, have been unable to compensate the negative influence of the modified convection flows in the glass melt. Increasing the temperature in the melting zone for the purpose of decreasing the number of cords has not been successful.

The significance of the effect of convection flows on the formation of cords in glass was corroborated after the introduction of an air-lift system in the quellpunkt zone, when the quantity of cords decreased nearly by half. However, the periodic swirling process and the limited number of bubbling nozzles do not provide for complete elimination of cords in strontium glass.

In our opinion, the next activity intended to decrease the quantity of cords should be a modification of the chemical composition of strontium glass. In this context it is necessary to compare the chemical composition of glass produced in the glass-melting furnace of the previous design and that of the glass produced in the new tank furnace (Table 1).

It can be seen that the new strontium glass does not contain CaO and $F_2$, whose place has been taken by ZnO and $ZrO_2$.

The removal of CaO has made its possible to decrease the propensity of glass for crystallization and to create conditions for increasing the content of SrO and BaO in the glass composition, which has significantly raised the x-ray absorption coefficient. For the same purpose ZnO and $ZrO_2$ have been introduced into the glass composition.

The new strontium glass has a decreased content of high-melting oxides: $Al_2O_3$ has decreased from 3.85 to 2.00% and $SiO_2$ from 63.25 to 61.70%. These modifications have a positive effect on the mechanical properties of glass, its chemical resistance, and x-ray absorption.

A different situation arises when the fluorine-bearing components are removed from the batch. It is known that fluorides together with other batch components form low-melting eutectic mixtures, which decreases the temperature of the liquid phase formation, intensifies the rates of dissolution of quartz particles and formation of silicates, increases the gas bubble size, and facilitates their rise to the melt surface [9, 10]. Furthermore, fluorides expand the temperature interval of product formation.

The positive effect of fluorides on the glass-melting process is mainly due to the fact that the fluoride ion participates in the destruction of the bridge bonds between silicon and oxygen and thus accelerates the glass-melting processes [10]:

$$\equiv Si - O - Si \equiv + NaF \rightarrow \equiv Si - O - Na^{+} F - Si \equiv.$$

The removal of fluorides from the batch composition has been motivated by the fact that they cause erosion of refractory materials and contaminate the ambient environment. However, other batch components release much more volatile components polluting the environment and reacting with the refractory materials of the furnace. The insignificant content of fluorine in the batch does not play a deciding role in the total quantity of components released in glass melting.

In our opinion, addition of a small quantity of fluorides to the batch for the new strontium glass will make it possible to lower the batch melting temperature and accelerate the silicate formation processes, which will decrease the quantity of cords.

Thus, the main reason for the formation of cords in melting electrovacuum strontium glass in a flame regeneration tank furnace without a barrier in the melting zone is related to the modification of convection flows in the bottom layers of the glass melt. A substantial part of cooled and more viscous glass melt moves rectilinearly towards the furnace neck without rising in the quellpunkt zone. Due to the significant decrease in the melt temperature in the lower layers of the deep tank and the shorter stay of the melt in the high-temperature zone, as well as due to the heterogeneity of the batch, the products of reactions of the melted batch with the refrac-

tory materials do not have time to fully dissolve and mix with the bulk of the glass melt and, therefore, produce cords.

To decrease the number of cords, it is advisable not only to install bubbling nozzles in the quellpunkt zone, but also introduce 0.15 – 0.20% fluorine.

In designing new furnaces it is necessary to take into account the effect of the modification of the furnace structural elements and the process parameters on glass melt convection flows.

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